Nano-Scale Surface Characterization of Poly (Ethyleneterephthalate) - Silicon Rubber Copolymers using Atomic Force Microscopy

Dr. Abduelmaged Abduallah, Dr. Kamal M. Sassi, Dr. Mustafa T. Yagub

Department of Chemical Engineering - Faculty of Engineering, Sabratha University, Sabratha, Libya

ABSTRACT

Atomic force microscopy has been used to investigated the surface properties of different materials, in this paper it is used to measure the surface roughness and surface adhesive force of three different membrane samples Poly (ethyleneterephthalate) (PET), Silicon Rubber (SR) and PET-SRcopolymers. This analytical method allows images representing the topography and adhesive force (Phase image) of the surface to be captured simultaneously at a molecular (nanometer) resolution. The distribution of hydrophilic (polar) groups and the surface roughness on the investigated surfaces ofthese membrane samples influences the subsequent processing of polymeric membrane manufacture as well as their performance. From the results a clear distinction was observed between the three samples in both images the topography (surface roughness) images and adhesive force images. Promising result were obtained for the PET-SRcopolymer samples to be a good candidate in membrane separation applications. This study may also help to explain the differences in membrane performances and efficiency during applications in the separation process.

KEYWORDS: PET, Silicon Rubber, Roughness, Topography Phase Image

1. INTRODUCTION

In the area of chemical and process engineering and environmental protection, a very significant technology is the process of separation by polymeric membranes. Membranes are most usually thin polymeric sheets, having pores in the range from the micrometre to sub-nanometre, that act as advanced filtration materials [1-3]. In general, five major membrane processes, including microfiltration, ultra filtration, reverse osmosis, electro dialysis and gas separation have found use in such applications[1-4].

A membrane is a perm selective barrier that allows particular species to pass through it while posing a partition for non-selective species. The active area of the polymer membrane to carry out the process of separation is the surface. The properties related to the surface are important for performing the separation process. Properties such as the pores size distribution, long-range electrostatic interactions and surface roughness are factors that determine the efficiency of polymer membrane for this application. It is thought that the surface roughness of the polymer membrane is a factor proportional to the bond strength of the membrane. The higher roughness leads to greater adhesive strength of the membrane and greater efficiency in the separation process [5].The intermolecular forces present in various chemical function and structures are the main cause of adhesion forces. In addition to the cumulative magnitudes of these intermolecular forces, there are also certain emergent mechanical effects[6].The solubility parameter theory, based on free energy of mixing, implies that the preferential sorption takes place when the solubility parameters of both polymer and the per meant species are very close. Another important factor is the interaction parameter that determines the affinity of a polymer for a particular species[7].

Surface roughness is often described as closely spaced irregularities or with terms such as 'uneven', 'irregular', 'coarse in texture', 'broken by prominences', and other similar ones[8]. Similar to some surface properties such as hardness, the value of surface roughness depends on the scale of measurement. In addition, the concept of roughness has statistical implications as it takes into consideration factors such as sample size and sampling interval. It is quantified by the vertical spacing of a real surface from its ideal form. If these spacing are large, the surface is rough; if they are small the surface is smooth.

Atomic force microscopy (AFM) is one means of imaging objects of dimensions from about the wavelength of light to those below a nanometer. Thus, in the case of membranes, it is possible to visualize the membrane surface properties, such as pores and morphology, using AFM. Fortuitously, the

size range of objects that may be visualized by AFM corresponds closely to the size range of surface features that determine the separation characteristics of membranes. However, the separation characteristics of membrane interfaces do not depend solely on the physical form of surface features. The surface electrical properties and the adhesion of solutes to membrane surfaces may also have profound effects on separation performance. It is thus exceedingly fortunate that an Atomic Force Microscope may also be used to determine both of these additional controlling factors. Finally, means may be devised to quantify all of these controlling factors in liquid environments that match those of process streams. Atomic Force Microscopy (AFM) technique has been used for several years for revealing the surface heterogeneity of polymeric materials[9-12].

There are two types of image contrast mechanisms in intermittent mode [13].

➢ *Amplitude imaging*: It's an image contrast mechanism where the feedback loop adjusts the z – piezo so that the amplitude of the cantilever oscillation remains (nearly) constant. The voltages needed to keep the amplitude constant can be compiled into an (error signal) image, and this imaging can often provide high contrast between features on the surface[14].

➢ *Phase imaging*: The main characteristic of this mode is that the phase difference between the driven oscillations of the cantilever and the measured oscillations can be attributed to different material properties. For example, the relative amount of phase lag between the freely oscillating cantilever and the detected signal can provide qualitative information about the differences in chemical composition, adhesion, and friction properties.

The AFM method of choice for the study of the surface heterogeneity of a polymeric sample is determined by the characteristics of that sample, as demonstrated by p. Eatonet al in their work with a poly (methyl methacrylate) /poly (dodecyl methacrylate) binary blend[12].Then in 2007Liu, D. -L. et al have conducted a study concerning the effect of roughness on the adhesion using AFM to obtain optimal roughness for minimal adhesion for other types of materials [6]. Poly (ethyleneterephthalate) (PET) un-grafted and poly (ethylene terephthalate) -graft-polystyrenegrafted PET-g-PST membranes were investigated by Khayet, M. et alfor organic/organic separation.[15].It was found that PET-g-PST membranes exhibited better selectivity than the un-grafted PET membrane while the permeation fluxes of the grafted membranes were lower. Recently Rychlewska, K. et alhave conducted study using Silicon Rubber (SR) membranes and applied this polymer for pervaporative desulfurization of gasoline [16]. SR possesses an SP of 15.5 kJ$^{1/2}$.cm$^{-3/2}$, and hence, is perfectly suitable for the preferential transport from gasoline. In fact, developed Silicon Rubber-based membranes have been found to possess significantly high flux for the desulfurization of thiophene-n-octane gasoline, as reported by Cao et al. [17].

In order to improve the stability and performance of SR membranes, and selectivity of PET various techniques are attempted such as polymer blending, copolymerization and inorganic particles incorporation, especially in the nano range. Multi-component polymer materials (copolymer, blend and composite) are widely used in many industries because by appropriate mixing of different materials one can

design ultimate material with the desirable properties. The structure-property relationship in such materials is difficult to understand without microscopic analysis. AFM is very helpful in this analysis at scales from hundreds of microns to nanometers. In this study the surface of PET, SR and segmented PET-SR copolymers are fully investigated using AFM. Furthermore, we explore the complementarily of the techniques of adhesion force mapping and topology mapping as a readily accessible means of probing the surface features of heterogeneous surfaces. This study will also provide a better understanding of the effect of roughness on the adhesion when working in the nano-scale. On this scale the effects of adhesion are significant in applications of separation systems.

2. Experimental Work
2.1. Samples Preparation
Two thin flat sheet of the each studied polymers (PET, SR and the segmented PET-SR copolymers as shown in the Table 1) were cut carefully from the polymer membrane with knife or blade (previously cleaned with is opropanol to prevent oil contamination often present on new steel blades). When selecting samples for analysis sample areas that are free of visible defects, like scratches or stains was chosen. Then membrane samples were rinsed three times with saturated pure water, and then the samples were placed inside furnace at 35 °C temperature for 24 hr, then rinsed three times with saturated pure water, stored completely immersed in saturated pure water at 15 °C at least 24 hr prior to measurement. To fix the flat sheet sample on the sample holder two-sided tape was used.

Table 1 Characteristics of investigated samples

Sample	PET (wt %)	Molecular Weight	Polydispersity
PET	100	2.8x10^5	4.6
PET-SR 001-002	25	3.2x10^5	6.4
PET-SR 001-200	50	3.7x10^5	5.8
PET-SR 100-200	75	3.6x10^5	6.2
SR	0	1.9x10^6	6.0

2.2. Characterization techniques
The pulsed-force mode of the atomic force microscopy (PFM-AFM) [20] was used to measure the surface energy (the adhesive force) of the copolymer surfaces. In this mode the AFM is operated in contact mode, and at the sometime a sinusoidal modulation is applied to its Z-piezo. Each image was recorded with a scan size of 20 x 20 µm^2 4x 4µm^2 and 2x 2 µm^2. The same tip was usedfor the entire series to avoid inconsistencies due to a variation in tip radii or spring constants. The adhesive force (F) is calculated using the following equation:

$$F = V \times k \times S \tag{1}$$

where V is the average voltage value from the adhesion images,

k is the spring constant (= 50 N/m) of the cantilever

and S (= 500nm/V) is the sensitivity of the photodiode.

The adhesive force was determined as an average of five adhesion images; each image of these images consists of 256 x 256 single measurements in the observed areas.All experiments were carried out under ambient conditions. The

scan rate was set in the range of 0.5 to 0.7 Hz.Only noise and image artefacts were eliminated using lowpass filtering.

From the topography images associated with the adhesion images in the pulsed force mode, the surface roughness was measured. The mean roughness (Ra) is the arithmetic average of the surface height deviation from the mean plane [21]. Ra is calculated according to the following equation:

$$Ra = 1/n \left(\sum_{i=1}^{n} |Zi| \right) \qquad (2)$$

The surface roughness of the copolymers was measured as an average of five different places on the surface of each copolymer in an area of 5 x 5µm^2.

The total adhesion force in this case; the contribution of all molecules involved in theprocess; can be described by the equation[19]:

$$F = 2\pi\omega R \left[\frac{R_q}{R + R_q} + \left(\frac{h_c}{h_c + R_q} \right)^2 \right] \qquad (3)$$

where: R = tip radius;

R_q = RMS of roughness;

h_c = distance separating the tip/sample,

and$2\pi\omega R$ represents the strength of the AFM system.

The total force is normalized by the surface energy so that ω is the work of adhesion force. The adhesion force falls with increasing surface roughness and also with increasing radius of the tip used in AFM.

3. Results and discussion
3.1. Surface Morphology and Surface Roughness
AFM images obtained on PET sample and SR sample in an area of 20µm square and 2µm square are shown in Figure 1. The image in Figure 1 (a, c) shows the overall surface morphology of the PET sheet and SR sheet, respectively, while the Figure 1 (b, d) shows high resolution of the surface morphology of both homopolymers sheets, respectively. The general morphology that found in both membrane sheets are pores surface with some regions contains more pores than others in the case of the PET sample and even distribution for the pores in the scanned surface of the SR sample.
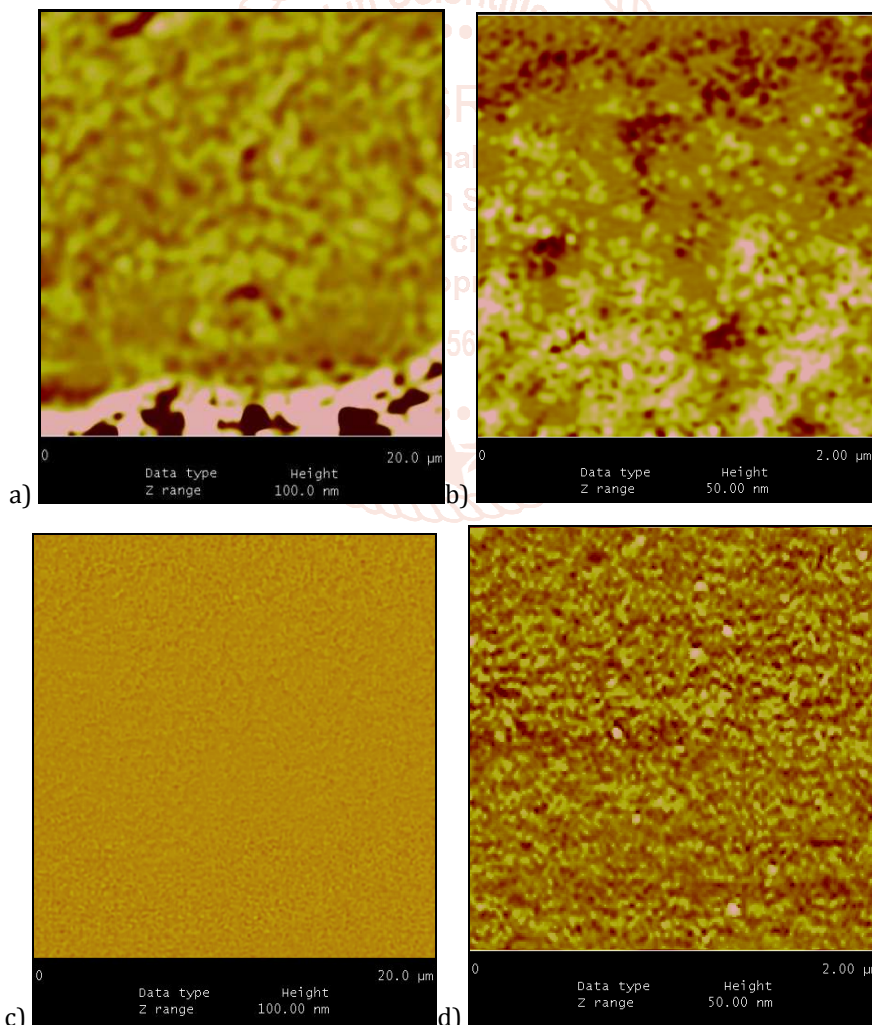

Figure 1: Surface morphology of PET membrane sheet (a, b) and SR membrane sheet (c, d).

AFM images obtained from scanning the PET-SR copolymer samples in an area of 20and 2µm square are shown in Figures 2. Figures 2 (a, b) for the PET-SR copolymer with 25 wt% SR while Figures 2 (c, d) for the PET-SR copolymer with 60 wt% SR. Once again the images for both copolymer samples surface showed pores type of topology with quite even distribution but less that that for the SR sample. When the PET distributed on the copolymer chains evenly the homogeneity of the copolymers becomes better, which leads to good distribution of the pores.
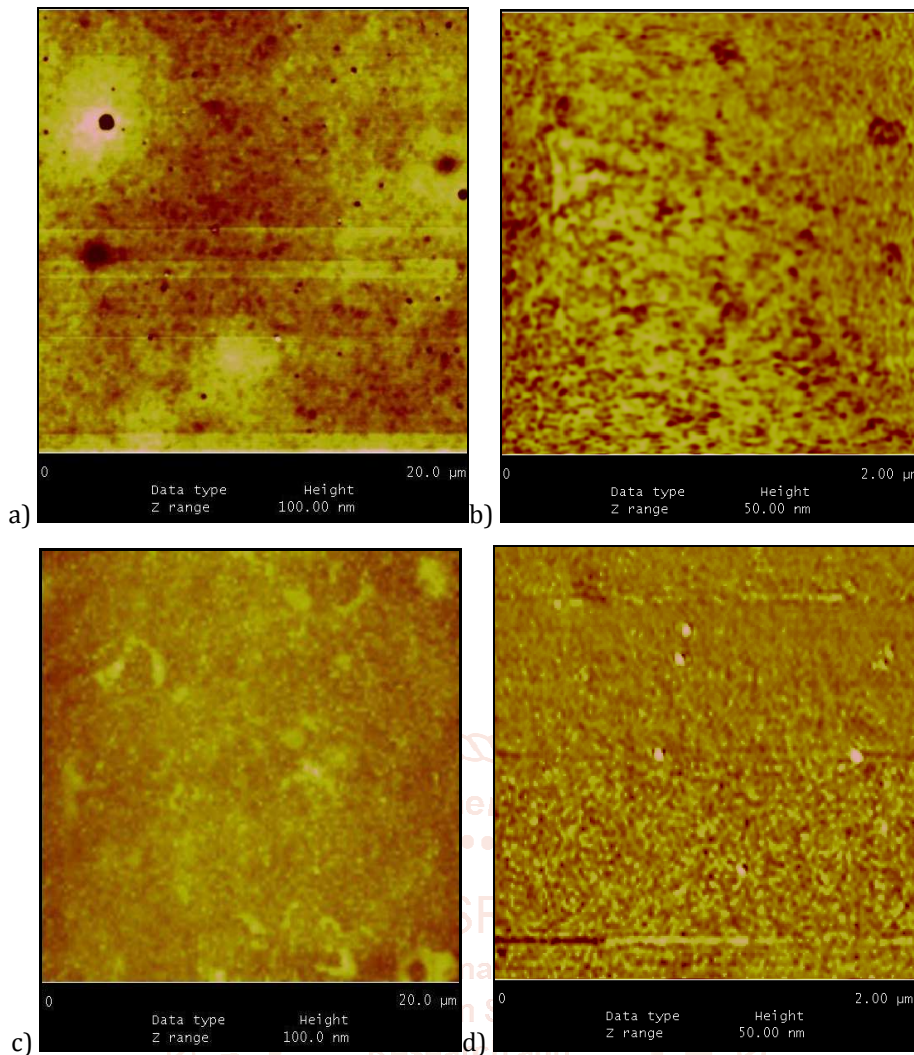
Figure 2: Surface morphology of PET-SR copolymer sheets with (a, b) 25 wt%SR and (c, d) 60 wt% SR.

Figure 3 shows the surface roughness for both PET and SR homopolymers as well as the PET-SR copolymers and the influence of varying SR content on the surface roughness of the PET-SR copolymers. It seems that the surface roughness value for PET is quite larger than for the SR, which might be due to the spherulitic crystal structure that usually present in this type of polymer. However for the copolymer samples the surface roughness is less than that for the PET homopolymer but larger than the SR surface roughness. The value of the surface roughness increases with increasing the Silicon Rubber content in the copolymer, which may be related to increasing in the phase separation on the surface as the Silicon Rubber content increases, where the SR segments or domains form islands on the surface. The size and the height of these islands increases as the SR concentration on the copolymers surfaces increases. The surface composition of these copolymers seems to depend on polymer structure, which affects the adhesive force, as well as the surface roughness.
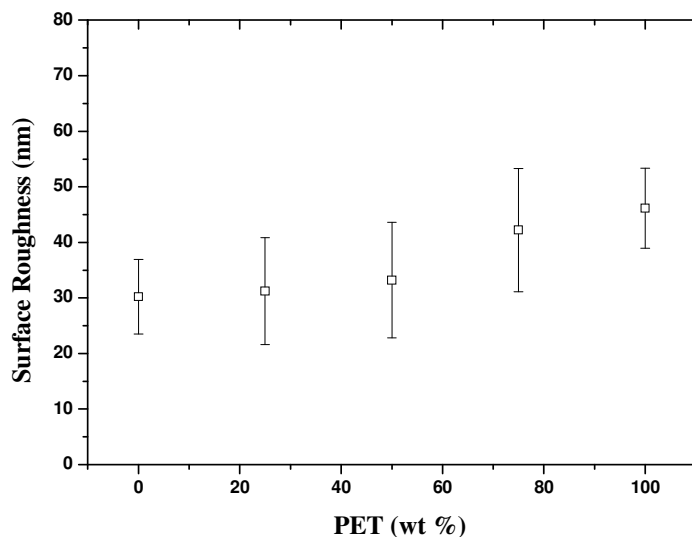

Figure 3: Surface roughness of the PET, SR and PET-SR copolymer treated and untreated samples.

Figure 3 shows a non-linear relationship between the average surface roughness and SR content. The changes in the surface roughness due to SR content has been reported before for polysiloxane-block-polyimides by Furukawa and co-workers [20, 21].The changes in the surface roughness was related to the degree of phase separation in the copolymer, which cannot be done in the PET-SR systems due to the fact that in addition to the phase separation effect, the crystallinity has great effect on the surface roughness. However for similar crystallinity degree sample slight indication could be drawn to the degree of phase separation.

Overall, based on the AFM images and data, the PET membrane may be characterized as a relatively rougher membrane than Silicon Rubber membrane. This observation is supported by the 3D rendered phase image of the membrane surfaces (Figure 4).
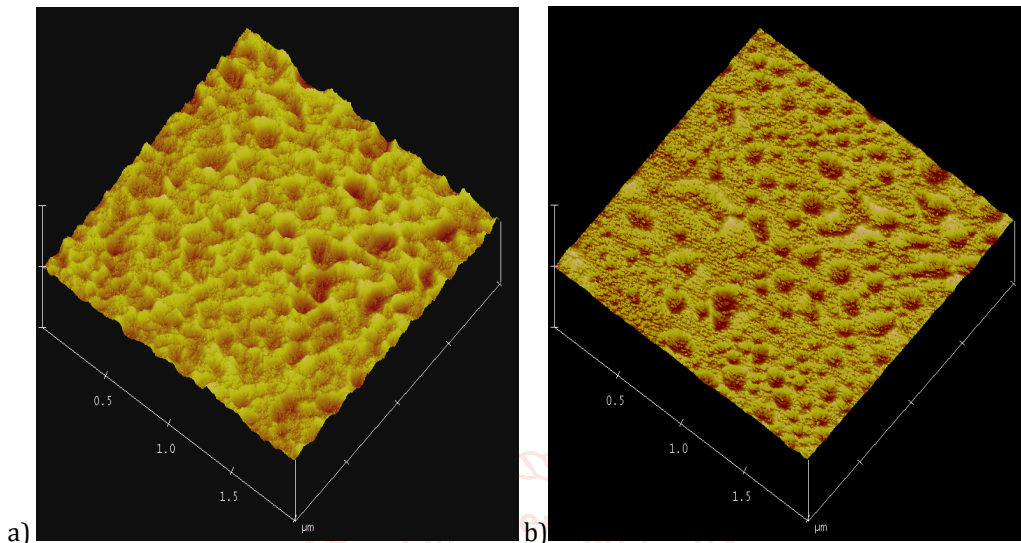

Figure 4: 3D phase image of the membrane surfaces (a) PET membrane sheetand (b) Silicon Rubber membrane sheet.

3.2. Adhesive force

A typical example of the AFM adhesive force image of a PET-SR copolymer (PET-SR 001-002) and the corresponding distribution histogram is shown in Figure 5. The image that included in the figure, is related to the phase images which is usually called adhesive force image. The dark spots in the adhesive force images indicate lower surface energy regions, which in our case is more likely to be related to the PET area, as it was suggested by Jin Z et.al. for poly (imidesiloxane) copolymers [22].

PET has low surface energy while Silicon Rubber has a very low surface energy, the PET-SR copolymers would be, therefore, expected to have a low energy surface, due to the SR surface segregation.
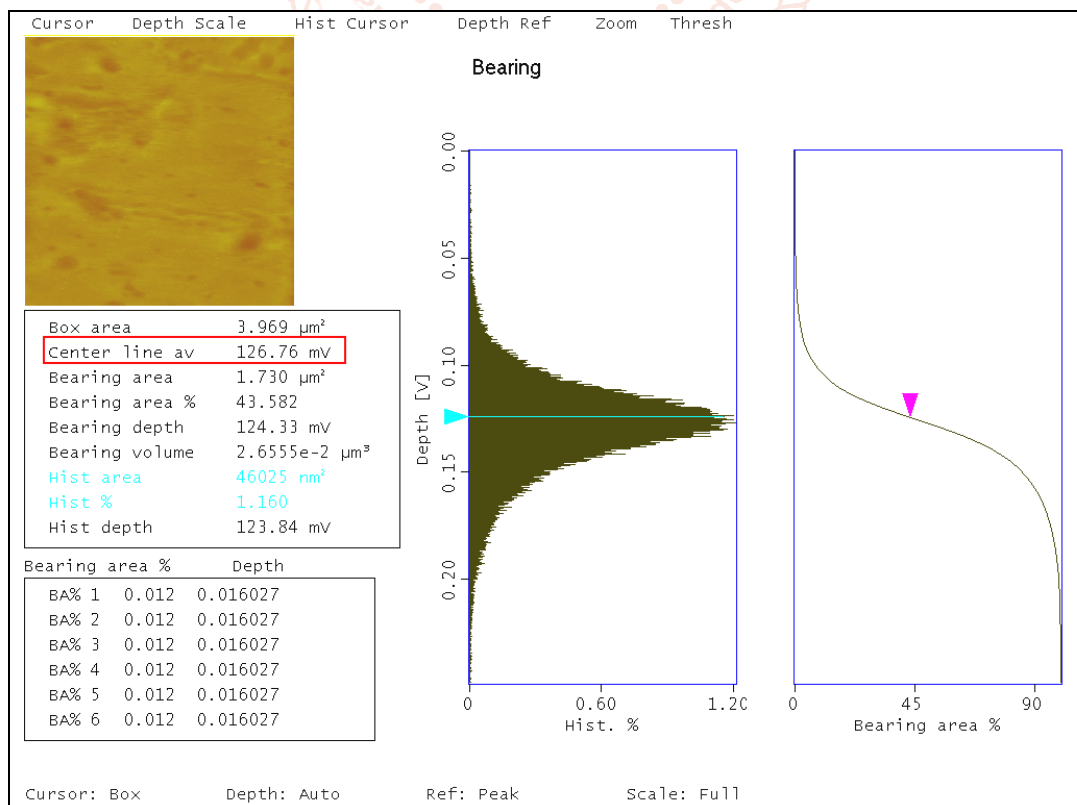

Figure 5: Typical examples of the AFM adhesive force image of a PET-SR copolymer and the corresponding voltage distribution histogram.

The surface energy (adhesive force) of PET-SR copolymers was measured using digital pulsed-force mode AFM (DPFM-AFM), and the average of the adhesive force is calculated and plotted against the SR content as it is shown in Table 2.

Table 2 The average and standard deviation of the adhesive force for the investigated membrane samples measured by AFM (DPFM-AFM).

Sample	Average Value of the Adhesive Force (nN)	Standard deviation
PET	244	45
SR	362	42
PET-SR 001-002	277	120
PET-SR 001-200	320	97
PET-SR 100-200	360	72

This table shows that as the Silicon Rubber content increases so the adhesive force decreases in the copolymer series. Additionally, minimization of the adhesive force in the series as the SR content increases is a result of an enrichment of the surface with SR segment. This was also observed from the AFM phase images. This result is consistent with results reported in literature for other SR copolymers[23-25].

The large standard deviation in both copolymers might be due to the diversity in the surface composition or in the function groups on the surface (such as CH_3, CH_2, C=O and OH), which could be used to investigate the possibility of forming complete monolayer of SR on the copolymers surface so the large variation in both samples is clear evident that no complete monolayer of SR has been formed on the surface of PET-SR copolymer, otherwise and in case of complete monolayer is formed the diversity of the function group will be less and therefore the standard deviation will be smaller. This confirms results obtained for perfectly alternating copolymers with b is-A sulphone, aromatic ester, urea and imide structures. The authors reported that a SR with M_n of between 6800 and 12000 g/mol was required to form a complete siloxanemonolayer[26].

The drastic difference in the adhesion energy hypotheses blending moduli for the monolayer and multilayered of the PET-SR copolymer membranes may lead to a transition in the morphology of the membranes on a corrugated surface, which in turn leads to a considerable difference in the measured adhesion energy [27].

4. Conclusion

Topographic mapping and adhesion force mapping (Phase image) have been combined to examine the surface features of heterogeneity in a Polyethyleneterephthalate (PET), Silicon Rubber (SR) blended film structure using AFM.

An extensive experimental investigation conducted to check the veracity of adhesive forces on silicon wafers with varying roughness. It was found that the adhesive forces between an AFM tip and the fractal surfaces decreased as the roughness exponent increases.

This work should help minimize adhesion station and progress the understanding of nanoscale contact mechanics. In the near future, the effects of surface roughness on the morphology and adhesion energy of substrate-supported membranes will be analyzed by a theoretical model of van der Waals interaction by our research group. This may shade

more light on the subject and may confirm the above-mentioned explanation for the considerable difference in the measured adhesion energy. In the case of both SR and PEThomopolymers the function groups variations on the surface is very limited and thus the standard deviation for both samples is very small.

5. References

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